Consumer and Corporate Affairs Canada
Consommation et Corporations Canada

(11) (A) No. 1 269 859

(45) ISSUED 900605

(52) CLASS 71-23
C.R. CL. 71-35

(51) INT. CL.[4] C05C 1/00,3/00,5/04

(19) (CA) CANADIAN PATENT (12)

(54) Ammonium Thiosulfate-Containing Fertilizers

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(21) APPLICATION No. 499,118

(22) FILED 860107

(30) PRIORITY DATE (US) U.S.A. (689,649) 850108

No. OF CLAIMS 13 - NO DRAWING

Canada

499118

AMMONIUM
THIOSULFATE-CONTAINING
FERTILIZERS

ABSTRACT

A fertilizer material, particularly in a solid particulate form, incorporating ammonium thiosulfate with a source of nitrogen, such as urea, urea ammonium nitrate, ammonium phosphate, ammonium nitrate, calcium nitrate or ammonium sulfate, and a process for preparation thereof. The fertilizer supplies necessary nutrients to the soil, and in addition inhibits urease and nitrification losses from the soil. The solid fertilizer is prepared by mixing the liquid ingredients at elevated temperature, and then flash cooling the liquid mixture under vacuum at elevated temperature. Drying may be completed by air drying under ambient conditions or in a vacuum oven.

BACKGROUND OF THE INVENTION

This invention relates to agricultural fertilizer materials, and, more particularly to a fertilizer containing ammonium thiosulfate.

Fertilizers are used in agriculture to supply macro and micro nutrients to the soil and thence to the growing plants. Most fertilizers supply one or more of nitrogen, phosphorus, potassium, and sulfur, and in addition may supply elements needed by the plants in trace amounts, such as iron, copper, zinc, and other nutrients. A farmer obtains a soil analysis for his fields, compares the available nutrient content with that required to grow the desired crops, and then either purchases a ready-made fertilizer or obtains a custom-blended fertilizer to meet the soil needs.

Many fertilizers may be produced in either a liquid or a solid form. The farmer selects the liquid or solid form for purchase based on several factors, including availability, the type of fertilizer application equipment that the farmer uses, and the objectives of the fertilization program. It is therefore highly desirable to manufacture particular fertilizers in both solid and liquid forms, to increase the available market and convenience to the consumer.

Fertilizers are typically prepared in the liquid form to achieve homogeneous mixtures and reactions where necessary. Solid fertilizers are then prepared from the liquid fertilizer material. In some instances, the preparation of the solid fertilizer is simple and straightforward, such as by dehydrating the liquid fertilizer to a solid particulate, and then crushing and granulating the particulate. In other

instances, the dehydrating operation may cause undesirable reactions in the fertilizer, such as the loss of one or more constituents, as by volatilization or precipitation. The inability to prepare a particular fertilizer in solid form is a serious disadvantage both for the farmer and for the fertilizer producer.

Although fertilizers are used to augment and increase the natural levels of nutrients in the soil to support high volume agriculture, the application of fertilizers represents only one part of the complex chemistry of the soil and the growing plant. Once the nutrients are placed into the soil either naturally or by a fertilizer, a portion of the nutrients is converted into a form that may be utilized by the plant and ingested into the plant, while another portion of the nutrients may be lost from the soil and thence unavailable to the plant. Such nutrient losses are undesirable, since they drain the soil of its naturally occurring nutrient material and in addition deprive the plants of a portion of the nutrients provided in the fertilizer. Nutrient losses may occur in many different ways, including leaching by water from the soil, volatile loss to the air, and chemical and biological reactions in the soil which promote and accelerate other loss mechanisms or convert the nutrients to a form unusable by the plants.

One of the single most important and universally required nutrients is nitrogen, provided in a form which may be utilized by the plant. Nitrogen is typically supplied as ammonia or urea, or a compound thereof, which may be conveniently manufactured and transported, and, when applied is readily utilized by the plants. Although nitrogen is required by the plants and

is readily provided in fertilizers, unfortunately the rate of nitrogen loss from the soil prior to uptake by the plants can be large. It is estimated that as much as 10% - 65% of the nitrogen may be lost before it reaches the plant, by leaching, volatilization, and, particularly, by bacterial reactions in the soil. Nitrogen loss occurs principally by two mechanisms. In the first, nitrogen in the form of ammonia is oxidized in a nitrification reaction by bacteria in the soil to form a volatile or leachable nitrate. In the second, nitrogen in the form of urea is hydrolyzed to ammonia gas, a reaction accelerated by the presence of urease enzyme. Nitrification and urease inhibitors are therefore desirable fertilizer additions, since they improve fertilizer efficiency, reduce ground water pollution by nitrates, increase crop yields, and allow the farmer to more effectively manage his time by applying fertilizer at his convenience.

A great deal of effort has been devoted to finding ways to inhibit nitrogen loss from the soil. Existing techniques are generally too expensive for widespread agricultural use, use volatile inhibitors so that application procedures are limited, and may depend upon the use of dangerous, environmentally damaging, chemicals. Known nitrification inhibitors having varying degrees of effectiveness include carbon disulfide, sodium trithiocarbonate, dimethyl disulfide, sulfa drugs such as sulfathiazole, thiourea, dicyandiamide, phenyl phosphorodiamidate potassium ethyl xanthate, [2-chlor-6(trichloromethyl) pyridine or nitrapyrin], and [5-ethoxy-3-(trichloromethyl)-1,2,4-thiadiazole]. The latter two chemicals are respectively marketed under the names of N-Serve* (by Dow Chemical Co.) and Dwell (by Olin Corporation).

* Trademark

N-Serve and Dwell are used primarily with liquid fertilizers, but in most cases the fertilizer must be incorporated into the soil immediately after the inhibitor addition to avoid decomposition and volatilization of the inhibitor. When these inhibitors are used with solid fertilizers such as granular urea, the inhibitor is typically sprayed onto the granule immediately before application, but volatilization losses are high due to the large, porous surface of the granules.

There have been attempts to incorporate nitrification inhibitors into solid fertilizers such as urea by cogranulation procedures. Solid urea is usually prepared by concentrating aqueous urea solution at temperatures reaching 280^{o}F - 300^{o}F, followed by granulation. Any inhibitor added to the solution must therefore be stable at these temperatures. Tests have shown that dicyandiamide, thiourea and phenyl phosphorodiamidate, may be thus cogranulated with urea to form a solid fertilizer, but use of these inhibitors has drawbacks such as high cost, easy volatilization, and possible carcinogenic character.

There therefore exists an ongoing need for improved fertilizer materials, which provide important nutrients in usable form and may be manufactured as either a liquid or a stable solid. Such fertilizers would preferably inhibit nitrogen loss from the soil by a safe approach using an inhibitor incorporated into the soil. In particular, there has existed a need for such a fertilizer which supplies nitrogen and sulfur to the soil, since these elements are sometimes required to meet particular nutrient needs. The present invention fulfills this need, and further provides related advantages.

SUMMARY OF THE INVENTION

The present invention provides a fertilizer containing sulfur and nitrogen in biologically usable form, and a process for preparing a solid particulate fertilizer which prevents volatilization and loss of sulfur during preparation. The fertilizer material is found to inhibit urease and nitrification losses from the soil, thus improving the efficiency of the fertilizer addition as well as improving the overall efficiency of the soil in providing nutrients to the plants.

In accordance with the invention, a fertilizer material comprises a substantially uniform mixture of ammonium thiosulfate and at least one source of nitrogen, preferably selected from the group consisting of urea, urea ammonium nitrate, ammonium phosphate, ammonium nitrate, calcium nitrate, and ammonium sulfate. In its solid particulate form, each particle comprises a substantially uniform mixture of ammonium thiosulfate and the nitrogen source. The ratio of the nitrogen source and the thiosulfate is not critical, but preferably the ammonium thiosulfate is present in an amount of at least 5% by weight of the final product. As little as 0.2% ammonium thiosulfate is effective in inhibiting urease and nitrification losses, but such small amounts are agriculturally not practical, if sufur is being added as a nutrient.

In another aspect of the invention, a solid fertilizer material may be prepared by mixing together ammonium thiosulfate and the source of nitrogen to form a liquid solution, at a temperature of no greater than about 180°F; and then applying a vacuum to the liquid solution to remove water therefrom, at a temperature of no greater than about 180°F, to form a solid particu-

late. At temperatures greater than about 180^{o}F, the ammonium thiosulfate decomposes. Optionally, small amounts of water may be added to assist in forming a liquid mixture when the ammonium thiosulfate and the source of nitrogen are mixed together at elevated temperature. Agitation and continued mixing during vacuum evaporation accelerate the production of the solid. The last stages of the vacuum evaporation of water proceed relatively slowly, and it is preferred to complete the drying by ambient air drying or at elevated temperatures in a vacuum dryer. The final drying should not be accomplished at elevated temperature in air, since sulfur is precitated from the fertilizer material. Finally, the dried particulate solid is crushed and screened to produce granules of a desired size distribution.

It will now be appreciated that the present invention represents an advance in the field of fertilizer manufacture and utilization. A fertilizer containing nitrogen and sulfur in usable form, and supplied by relatively inexpensive ingredients, may be prepared as either a liquid or solid, without a substantial loss or precipitation of sulfur during manufacture. When applied, the fertilizer material inhibits nitrogen loss from the soil, to achieve increased efficiency. Other features and advantages of the present invention will become apparent from the following more detailed description, which illustrates, by way of example, the principles of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The raw materials utilized in the fertilizer process and material of the preferred embodiments of the present invention are readily obtained commercially. Ammonium thiosulfate having a nominal composition of grade (12-0-0-26 S) was obtained from J. R. Simplot Company, Brandon, Manitoba, Canada. The conventional N-P-K-X agricultural notation is used herein, where N denotes nitrogen, P denotes phosphorus, K denotes potassium, and X represents other elements, here sufur.) The commercial product was found to contain about 57 weight percent ammonium thiosulfate, 38 weight percent water, 2.5 weight percent ammonium sulfate, and 2.5 weight percent ammonium sulfite. Urea-ammonium nitrate of grade (28-0-0) was obtained from J. R. Simplot Company, Brandon, Manitoba, Canada. Solid pure urea was obtained from J. R. Simplot Company, Pocatello, Idaho. Operability of the present invention does not require the use of ingredients of high purity or other special characteristics.

In accordance with one aspect of the invention, the liquid ammonium thiosulfate and the source of nitrogen, preferably urea or urea-ammonium nitrate, are mixed together to form a substantially uniform mixed solution at a temperature of no greater than about $180^{\circ}F$. In preparing the mixed solution, no observable chemical reaction occurs. There is no known limitation on the ratios of the ammonium thiosulfate and the source of nitrogen in the solution, but a typical solution is prepared by mixing about 100 parts by weight of the liquid ammonium thiosulfate solution with about 950 parts by weight of urea. Since the ammonium thiosulfate solution contains about 57 weight percent ammonium thiosulfate, the resulting uniform mixed solution

contains about 950 parts urea, 57 parts ammonium thiosulfate, 38 parts water, and 5 parts impurities. This concentration amount of ammonium thiosulfate is found to be effective in inhibiting nitrification reactions in soils, as will be described more fully below. Other ratios of ammonium thiosulfate have varying effects, but all ratios examined have been found effective in inhibiting nitrification of soils to which the fertilizer material is added.

In accordance with another aspect of the invention, a solid fertilizer includes particles each comprising a substantially uniform mixture of ammonium thiosulfate and a source of nitrogen, the source of nitrogen preferably being urea. Such solid mixtures have been previously impossible to prepare, due to volatilization and loss of sulfur during dehydration and drying of a liquid mixture of the ingredients to form a solid. In a process for preparing the preferred ammonium thiosulfate-urea fertilizer material, the desired portions of ammonium thiosulfate and urea are mixed together to form a liquid solution at a temperature of no greater than about 180^{o}F, and then a vacuum is applied to the liquid solution to evaporate water therefrom, while maintaining a temperature of no greater than about 180^{o}F.

No limitations are known on the ratios of the ammonium thiosulfate and the urea in the solution. For example, the previously described liquid solution of 950 parts urea, 57 parts ammonium thiosulfate, 38 parts water and 5 parts impurities may be vacuum evaporated to yield a solid particulate having 950 parts urea, 57 parts ammonium thiosulfate, and 5 parts impurities (by weight), or slightly less than 95% by weight urea.

Urea and ammonium thiosulfate aqueous solution have limited mutual solubility at elevated temperatures. When more than about 95% by weight urea is utilized, a minor amount of water may be added to assist in preparing a liquid solution at a temperature of no greater than about 180°F. Typically, no added water is needed for a solution containing 90% by weight urea, while 5% water by weight is added to achieve solubilization for a mixture containing 5% by weight ammonium thiosulfate solution and 90% by weight urea. The excess water is present only to aid in forming the solution at elevated temperatures, and is evaporated in forming the solid. Mixing can occur in any suitable container, such as a metal or plastic vessel.

After the liquid mixture of ammonium thiosulfate and urea is prepared, it is processed to the solid form by applying a vacuum to evaporate water from the liquid mixture while controlling temperature to maintain the evaporating solution at a temperature of no greater than about 180°F. The evaporation is endothermic, and heat is typically added to maintain the temperature. The vacuum is preferably applied by a barometric condenser having a high capacity to allow removal of the water vapor. The condenser is preferably sized so as to maintain a vacuum of about 1-1/2 to about 4 inches mercury above the evaporating solution. (Higher or lower vacuums are operable but the indicated range is most commercially feasible to balance the cost of vacuum equipment required for higher vacuums against the slower evaporation kinetics of lower vacuums.) The vacuum evaporation is conducted in any suitable apparatus, such as a closed metal or plastic chamber.

The solution mixing and evaporation temperatures are preferably no greater than about 180°F. At

temperatures above about 180°F, sulfur is precipitated from the thiosulfate, thereby producing an undesirable product. At temperatures below about 180°F, the evaporation rate of the water is reduced, although the process remains operable. The solution mixing and evaporation temperatures are therefore selected to be no greater than about 180°F, and preferably about 180°F.

At the indicated temperature and vacuum, the vacuum evaporation proceeds rapidly. Preferably, the mixture is agitated by a mechanical mixer or other means during vacuum evaporation to accelerate the formation and drying of a solid. As an example, about 0.25 gallons of a mixture of 4.6% by weight ammonium thiosulfate, 87.9% by weight urea, and 7.5% by weight water was mixed together at about 180°F. The liquid solution was transferred into a 0.33 gallon capacity vacuum chamber, and then a vacuum of about 1-1/2 inches mercury was applied by a vacuum pump. Heat was supplied to the vacuum chamber during vacuum evaporation by an electrical heater. Sufficient heat was supplied to maintain the mixture at about 180°F during the entire vacuum evaporation process. After substantially all of the free liquid had evaporated, a clear particulate mass remained. It was observed that final drying of this particulate mass to a completely dry solid occurs slowly, so that, in a preferred approach, the particulate mass was removed from the vacuum container and dried to complete dryness in ambient air. It was found that placing the particulate mass into a low temperature drying oven in air resulted in decomposition and an undesirable precipitation of sulfur from the particulate mass. Therefore, use of an atmospheric pressure air drying oven to complete the drying operation is to be avoided. Drying may also be accomplished in a low-temperature vacuum oven.

To complete the preparation of the fertilizer material, the particulate mass is preferably crushed and sized. The solids may be crushed in any convenient approach, such as in a roll crusher. The crushed mixture is then graded by sizing screens to produce the desired distribution of granules for packaging. Particulate material having undesired product size may be redissolved and recycled through the process.

It has been found that the fertilizer of the invention has a particularly beneficial effect on inhibiting nitrification and urease reactions in soils. That is, application of the fertilizer reduces the loss of nitrogen from the soil, making more of the applied nitrogen available to the plants. In achieving this inhibition of nitrogen loss, the fertilizer of the present invention can replace far more costly nitrification inhibitors such as dicyandiamide, thiourea, phenyl phosphorodiamidate, and potassium ethyl xanthate. It also avoids use of carbon disulfide and related compounds, which are recognized as nitrification inhibitors, but which may be objectional due to flamability, unavailability, toxicity, and odor. Because of the very high volumes of fertilizer utilized, the cost savings based on use of ammonium thiosulfate are extensive.

In laboratory tests, soil samples were prepared by mixing 50 grams of a Williams Loam soil with 10 milliliters of water in a bottle. A 0.1 milliliter drop of a liquid fertilizer solution was placed on the soil surface and allowed to incubate for 28 days. Nitrogen loss was calculated and compared with nitrogen loss of a control sample, following the method described by Bremner and Bundy, 1974, <u>Inhibition of Nitrification in Soils by Volatile Sulfur Compounds</u>, <u>Soil Biol. Biochem.</u> 6:161-165.

The liquid fertilizers utilized in the study all included about 90% by volume urea ammonium nitrate, and ammonium thiosulfate in a range of 0, 1, 2, 5, and 10 percent by volume. For those fertilizers containing less than 10% by volume ammonium thiosulfate, the balance of the solution was water. Inhibition of nitrification after 28 days was found to be about 20% for the liquid fertilizers containing 1 and 2 percent ammonium thiosulfate, about 50% for the fertilizer containing about 5% ammonium thiosulfate, and about 60% for the fertilizer containing about 10% ammonium thiosulfate. It is believed that similar inhibition of nitrification results for solid fertilizers containing like amounts of ammonium thiosulfate in combination with the nitrogen source.

The use of ammonium thiosulfate in fertilizers rather than other nitrification inhibitors also has important agricultural value. The ammonium thiosulfate eventually decomposes to nitrates and sulfates, which have fertilizer value in themselves, whereas decomposition products of other nitrification inhibitors typically have no such fertilizer value in themselves.

As can now be appreciated, the fertilizer and process of the present invention provide important advantages to the farmer, in that a fertilizer which inhibits nitrification may be provided inexpensively, and in either a liquid or solid form. The process for preparing a solid fertilizer from ammonium thiosulfate and a nitrogen source avoids the loss of sulfur from the fertilizer by a vacuum evaporation process to remove water from the liquid mixture to form a solid, and then further vacuum evaporation or ambient temperature drying to form a dry particulate. Although a particular embodiment of the invention has been described for

purposes of illustration, various modifications may be made without departing from the spirit and scope of the invention. Accordingly, the present invention is not to be limited except as by the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS.

1. A process for preparing a solid fertilizer material, comprising the steps of:

mixing together ammonium thiosulfate and a source of nitrogen to form a liquid solution, at a temperature of no greater than about 180°F, the source of nitrogen being a salt or organic compound containing nitrogen;

applying a vacuum to the liquid solution to evaporate water from the liquid mixture, at a temperature of no greater than about 180°F to prevent loss of ammonium thiosulfate, to form a solid particulate.

2. The process of claim 1, wherein the source of nitrogen is selected from the group consisting of urea, urea-ammonium nitrate, ammonium phosphate, ammonium nitrate, calcium nitrate, and ammonium sulfate.

3. The process of claim 1, wherein the source of nitrogen is urea.

4. The process of claim 1, wherein the ammonium thiosulfate is present in an amount of at least about 0.2% by weight of the solid.

5. The process of claim 1, wherein the ammonium thiosulfate is present in an amount of at least about 5% by weight of the solid.

6. The fertilizer process of claim 1, including the additional step of:

crushing the solid particulate remaining after evaporation to produce granules.

7. The process of claim 1, including the additional step, after said step of applying, of

drying the solids remaining after evaporation in ambient temperature air.

8. A solid particulate fertilizer material, each particle comprising a substantially uniform mixture of ammonium thiosulfate and a source of nitrogen, the source of nitrogen being a salt or organic compound containing nitrogen.

9. The material of claim 8, wherein the source of nitrogen is selected from the group consisting of urea, urea-ammonium nitrate, ammonium phosphate, ammonium nitrate, calcium nitrate and ammonium sulfate.

10. The material of claim 8, wherein the ammonium thiosulfate is present in an amount of at least about 0.2% by weight of the solid.

11. The material of claim 8, wherein the ammonium thiosulfate is present in an amount of at least about 5% by weight of the solid.

12. The material of claim 8, wherein the source of nitrogen is urea.

13. A process for fertilizing and inhibiting nitrogen

loss from soil, comprising the steps of:

preparing a solid particulate material, each particle comprising a substantially uniform mixture of ammonium thiosulfate and a source of nitrogen, the source of nitrogen being a salt or organic compound containing nitrogen; and

applying the solid particulate material to the soil, whereby nitrogen and sulfur are provided to the soil, and nitrogen loss is inhibited.